Finite temperature electronic simulations beyond the Born-Oppenheimer approximation

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We introduce a general technique to compute finite temperature electronic properties by a novel covariant formulation of the electronic partition function. By using a rigorous variational upper bound to the free energy we are led to the evaluation of a partition function that can be computed stochastically by sampling electronic wave functions and atomic positions (assumed classical). In order to achieve this target we show that it is extremely important to consider the non trivial geometry of the space defined by the wave function ansatz. The method can be extended to any technique capable to provide an energy value over a given wave function ansatz depending on several variational parameters and atomic positions. In particular we can take into account electronic correlation, by using the standard variational quantum Monte Carlo method, that has been so far limited to zero temperature ground state properties. We show that our approximation reduces correctly to the standard Born-Oppenheimer (BO) one at zero temperature and to the correct high temperature limit. At large enough temperatures this method allows to improve the BO, providing lower values of the electronic free energy, because within this method it is possible to take into account the electron entropy. We test this new method on the simple hydrogen molecule, where at low temperature we recover the correct BO low temperature limit. Moreover, we show that the dissociation of the molecule is possible at a temperature much smaller than the BO prediction. Several extension of the proposed technique are also discussed, as for instance the calculation of critical (magnetic, superconducting) temperatures, or transition rates in chemical reactions.

I. INTRODUCTION

The calculation of finite temperature electronic properties is one of the most important and challenging aspects of the numerical simulations. In the past several progress have been done by extending the DFT method to finite temperature [1, 2] or by using quantum Monte Carlo [3] (QMC) within various path integral formulations [4–9], especially in the study of the hydrogen phase diagram [10–17]. In both cases many problems remain as for instance the lack of an accurate local functional at finite temperature for DFT methods prevents so far practical applications, and, within QMC techniques, the difficulty to deal with the fermion sign problem[18], restricts the spectrum of applicability to very few cases and very limited temperature ranges. On the other hand it is clear that, in many physical phenomena, such as the occurrence of magnetic or insulating phases below a critical temperature, the electronic entropy cannot be neglected, even when the small ratio λ_{ei} between the electronic mass and the atomic one, allows the decoupling of the electronic degrees of freedom from the atomic ones, within an acceptable approximation. In this paper we aim to extend the validity of the Born-Oppenheimer approximation in the following sense. By using the smallness of λ_{ei} we are generally lead to compute an electronic partition function $Z[\mathbf{R}]$ at fixed nuclei position:

$$Z = \int d\mathbf{R} \ Z[\mathbf{R}] \tag{1}$$

$$Z[\mathbf{R}] = \text{Tr} \exp(-H_\mathbf{R}/T) \tag{2}$$

where T is the temperature (here and henceforth the Boltzman constant is assumed to be one and we neglet for simplicity the overall constant coming from integration of the atomic momenta), $H_\mathbf{R}$ is the standard electronic Hamiltonian, that includes also the classical ionic contribution, and that depends only parametrically upon the atomic positions $\mathbf{R}$. Eq.(1) is the first step of the Born-Oppenheimer approximation that- we remark- is generally

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valid for λ_{ei} small, namely when the temperature T is large enough that quantum effects on protons can be neglected. The second approximation, usually adopted within the BO approximation, is to assume that the electronic degrees of freedom have a gap much larger than the temperature T so that $Z[\mathbf{R}]$ can be approximated by $\exp(-E_0(\mathbf{R})/T)$ where $E_0(\mathbf{R})$ is the ground state energy of the hamiltonian $H_{\mathbf{R}}$. In the following derivation we want to avoid the latter approximation, because, as emphasized before, in several cases it may fail even when we are in the limit of small λ_{ei}. For instance the occurrence of a broken symmetry phase often implies gapless electronic excitations in $H_{\mathbf{R}}$, and the approximation $Z[\mathbf{R}] = \exp(-E_0(\mathbf{R})/T)$ cannot be safely assumed. Other examples are conical intersections[19–21], when for some particular ionic positions $H_{\mathbf{R}}$ becomes gapless and nearby the proximity between different (namely corresponding to low-lying excited states) BO energy surfaces is possible. In this conditions a pure electronic ground state technique fails as the tunneling between different BO energy surfaces cannot be taken into account consistently. As the last very important example we mention the calculation of transition rates in chemical reactions, that cannot be accurately computed within a pure BO approximation[22–26].

The main task of this paper is to device a method, able to quantify finite temperature properties of realistic systems, within a rigorous variational upper bound of the total free energy $F = -T \ln Z$, in the limit of small λ_{ei}. The method we propose is supposed to be simple enough to avoid most of the known drawbacks, as does not rely on the knowledge of any particular functional, or, within our variational approximations, can be employed by quantum Monte Carlo, without facing the so called "fermion sign problem".

The paper is organized as follows. The derivation of the approximate expression of the electronic partition function introduced and used in this work is given in section II, and some important but more detailed aspects are reported in appendixes A, B, C and D. This derivation is not specific for a QMC framework, indeed App. D is specifically oriented to an implementation of the method into a Hartree-Fock or DFT framework. Next we show how to sample the introduced partition function using a Langevin dynamics for the wave function parameters, sections III, and the ion coordinates, section IV. In section V we finally show some results we have obtained using this approach for the hydrogen molecule.

II. FINITE TEMPERATURE ELECTRONIC PARTION FUNCTION

We consider the problem to estimate the finite temperature partition function of an electronic system with N electrons and M atoms, where we assume in the following that, as discussed in the introduction, the ions are classical particles, whose coordinates $\mathbf{R}$ appear just as simple parameters in the electronic hamiltonian $H_{\mathbf{R}}$ and are confined in a finite volume V. Therefore, once the ion positions are fixed, we need to evaluate the electronic partition function:

$$Z[\mathbf{R}] = \text{Tr} \exp\left(-\beta H_{\mathbf{R}}\right) \tag{3}$$

where $\beta = 1/T$. Our derivation applies for an Hamiltonian with a bounded spectrum defined in a finite Hilbert space with dimension D. For instance in electronic structure calculation one can consider a finite dimensional basis of localized orbitals around each atom. In order to simplify the notations we can consider standard creation operators with canonical commutation rules, spanning the finite single electron basis, as for a standard lattice Hamiltonian, namely $c_i^\dagger$ for $i = 1, \cdots, L$, where for shorthand notations i labels also the spin, namely $i \leq L/2$ ($i > L/2$) refers to spin up(down)-states. We consider the generic wavefunction $|\psi\rangle = J \times |SD\rangle$, where:

$$J = \exp(1/2 \sum_{i,j} v_{i,j} n_i n_j) \tag{4}$$

$$|SD\rangle = \left[\prod_{i=1}^{N} \sum_{j=1}^{L} \psi_j^i c_j^\dagger\right] |0\rangle \tag{5}$$

and $n_i = c_i^\dagger c_i$, for a system of N electrons. In the continuous limit this wave function is the standard Jastrow-Slater one used in quantum Monte Carlo in order to describe electron correlation[27]. Estensions of this wave function are possible using AGP[28], Pfaffian[29], backflow[30], and the following considerations apply also for these more recent ansatz, because they all contain the Slater determinant $|SD\rangle$ in a particular limit.

In all cases, the real variational parameters that define the above wave function, namely $v_{i,j}$ and ψ_j^i are compactly denoted by $\alpha \equiv \{\alpha_i\}_{i=1,\ldots,p}$ and since all physical quantities do not depend on the norm of the wave function, we consider the $\alpha-$manifold of states:

$$|\alpha\rangle = \frac{|\psi\rangle}{\||\psi\rangle\|} \tag{6}$$

The metric in this manifold becomes non trivial as, by a straightforward calculation, the distance between two states $|\alpha\rangle$ and $|\alpha + d\alpha\rangle$ is given by:

$$ds^2 = \||\alpha + d\alpha\rangle - |\alpha\rangle\|^2 = d\alpha^i d\alpha^j S_{i,j} \tag{7}$$

where summation over repeated indices is assumed, and S is a $p \times p$ matrix defining the metric tensor of this rather non trivial space, described by p independent variational parameters (e.g. a subset of $v_{i,j}$ and ψ_{ij}). The matrix S can be explicitly evaluated and depends only on average first derivatives of the wave function with respect to the parameters $\alpha's$:

$$S_{i,j} = \frac{\langle \partial_i \psi | \partial_j \psi \rangle}{\langle \psi | \psi \rangle} - \frac{\langle \partial_i \psi | \psi \rangle}{\langle \psi | \psi \rangle} \frac{\langle \psi | \partial_j \psi \rangle}{\langle \psi | \psi \rangle} \tag{8}$$

It defines a metric as it is strictly positive definite if all p variational parameters are independent and therefore its determinant $|S|$ is non vanishing. This matrix turns out to be exactly the one used in several optimization techniques[31, 32], and can be computed also for correlated systems by sampling the correlations of the quantities $O_j(x) = \frac{\langle x | \partial_j \psi \rangle}{\langle x | \psi \rangle}$ over the configuration space $\{x\}$ where electrons have a definite spin and positions, namely:

$$S_{i,j} = \langle O_i O_j \rangle - \langle O_i \rangle \langle O_j \rangle \tag{9}$$

where the symbol $\langle \ldots \rangle$ denotes average over a distribution $\Pi(x) \propto \langle x | \psi \rangle^2$, that can be sampled by standard variational Monte Carlo.

In Eq.(3), we use a simple relation for recasting the trace in a finite dimensional Hilbert space as an integral of normalized wavefunctions $|c\rangle = \sum_{i=1}^{D} x_i |i\rangle$, namely:

$$D \int dx^D \delta(\|x\| - 1) \langle c | \exp(-\beta H) | c \rangle = S_D \mathrm{Tr} \exp(-\beta H) \tag{10}$$

where $S_D = 2\pi^{D/2}/\Gamma(D/2)$ is the area of the $D-$dimensional unit sphere. We note that this simple relation can be used to establish within a rigorous mathematical framework the finite temperature Lanczos method used in Ref.33. In this technique finite temperature estimates of the partition function are obtained with a finite set of randomly generated states $|c\rangle$, once it is assumed that $\langle c | \exp(-\beta H) | c \rangle$, can be computed with high accuracy with the Lanczos method. Indeed this is nothing but evaluating statistically the integral in the LHS of Eq.(10), and one does not need any further assumption to validate the method, apart from the fact that error bars have to be computed with standard statistical techniques.

The simple relation (10) can be also extended in the space α with non trivial metric, by using the invariant measure $d\alpha^p \sqrt{|S|}$, corresponding to the metric tensor S:

$$\frac{\int d\alpha^p \sqrt{|S|} \langle \alpha | \exp(-\beta H_{\mathbf{R}}) | \alpha \rangle}{Z_S} = \mathrm{Tr} \exp(-\beta H_{\mathbf{R}}) \tag{11}$$

This relation is proven in App.A, provided the dimension of the space is large enough, namely contains at least the full space of Slater determinant wave functions, where the overall constant has been obtained by using that $Z[\mathbf{R}] = D$ for $\beta = 0$, as the metric normalization Z_S is defined as $Z_S = \frac{\int d\alpha^p \sqrt{|S|}}{D}$. We emphasize here that the relation (11) is *exact* even when the dimension of the space p is much smaller than the dimension of the Hilbert space. For instance for real Slater determinants the number $p < NL$ as they are defined by N orbitals each depending on L coefficients (see Eq.4), whereas the Hilbert space dimension D grows exponentially with L and N (See App.D for the parametrization of an arbitrary real Slater Determinant))

In practice the number p of variational parameters defining the wave function ansatz can be much smaller than that necessary to span all possible Slater determinants. In the case $p \ll NL$ we expect that the equation (11) is still valid but the trace in the RHS is limited to the largest subspace with dimension D_s spanned by the variational ansatz. Moreover a weak dependence on R in Z_S is also expected when a basis dependent on the atomic positions is used (it is not the case for a plane wave basis for instance). The calculation can be meaningful also in this case after a careful study of the dependence of the results upon the dimension of the basis chosen, as it is common practice in quantum chemistry calculations. In fact, in the limiting case when the one particle basis set used to define the orbitals in the Slater Determinant becomes complete the metric normalization Z_S is independent of R, because any change of basis is equivalent in this limit to a mapping $\alpha \to \alpha'$. Thus Z_S, being explicitly covariant, is independent of R and can be considered as an irrelevant constant. Therefore, within the completeness assumption, following the

simple derivation of App.B, we can easily bound the exact electronic partition function $Z[\mathbf{R}]$, because, due to the convexity of the exponential function, the expectation value of an exponential operator over a normalized state $|\alpha\rangle$ satisfies:

$$\langle\alpha|\exp(-\beta H_{\mathbf{R}})|\alpha\rangle \geq \exp(-\beta\langle\alpha|H_{\mathbf{R}}|\alpha\rangle).$$

This immediately provides a rigorous lower bound Z_Q for the partition function Z:

$$Z \geq Z_Q = \frac{\int d\mathbf{R}\int d\alpha^p \sqrt{|S|}\exp(-\beta\langle\alpha|H_{\mathbf{R}}|\alpha\rangle)}{Z_S} \tag{12}$$

and a corresponding upper bond F_Q for the free energy $F = -T\ln Z$:

$$F \leq F_Q = -T\ln Z_Q \tag{13}$$

In this way it is evident that F_Q represents an improvement to the standard Born-Oppenheimer (BO) approximation. In fact in this approximation only one state is assumed to contribute to the integral in Eq.(12), namely the lowest energy state of $H_{\mathbf{R}}$ within the ansatz given by $|\alpha\rangle$:

$$E_{BO}[\mathbf{R}] = \min_{\alpha}\left\{\langle\alpha|H_{\mathbf{R}}|\alpha\rangle\right\} \tag{14}$$

Indeed it is clear that $F = \min_{\mathbf{R}}\left\{E_{BO}[\mathbf{R}]\right\}$ only at $T = 0$, and represents a very bad approximation to F as long as the temperature is raised, whereas the approximate partition function F_Q approaches the correct large temperature limit $-T\ln(DV^M)$ of the exact partition function, while remaining a rigorous upper bound for any T.

In App.C we see in detail a comparison between the approximated partition function Z_Q here introduced, and the exact and BO ones, showing that our approximation turns out to be better than the BO one, above a temperature T^*, that remains meaningful in the thermodynamic limit.

III.   MONTE CARLO SAMPLING OF THE PARTITION FUNCTION Z_Q

In principle the partition function Z_Q can be sampled by almost standard Monte Carlo methods, whenever the metric S and the expectation value of the energy H over the ansatz $|\alpha\rangle$ are known, for instance within the Hartree-Fock theory, namely when $|\alpha\rangle$ represents just a simple Slater determinant. It is also possible to replace in Z_Q the expectation value of the energy with any DFT functional depending on $|\alpha\rangle$, through the corresponding density or gradient, the condition of functional minimum being recovered correctly at $T = 0$. For a discussion about the space of parameters for a Slater determinant wave function, and the introduction of an invariant measure in this space see App.D.

However in the truly correlated case, namely when the ansatz $|\alpha\rangle$ differs from a Slater determinant, there are extra complications because both the matrix S and $\langle\alpha|H_{\mathbf{R}}|\alpha\rangle$ are known only within statistical accuracy. In this case a possible way to sample the partition function Z_Q and corresponding thermodynamic quantities is to use the penalty method[34], introduced some years ago, by using a cost function

$$V_P(\alpha, \mathbf{R}) = \langle\alpha|H_{\mathbf{R}}|\alpha\rangle - \frac{1}{2\beta}\ln|S| \tag{15}$$

that can be computed statistically with corresponding error bars.

In the following we have chosen a different route, by employing a finite temperature molecular dynamics rather than Monte Carlo sampling, because recent quantum Monte Carlo packages provide efficient estimates of energy derivatives and ionic forces[35].

Our goal is to sample points in the electronic parameter space α distributed according to the probability distribution defined in Eq.(12), by using first order derivatives of the cost function. In the standard Cartesian metric it is common practice to use a Langevin dynamics for the variables $\{\alpha\}$ and $\{\mathbf{R}\}$, by means of the standard first order equation of motions (unit mass is assumed for simplicity)[36]:

$$\dot{\vec{x}} = -\partial_{\vec{x}}V + \vec{\eta} \tag{16}$$

where $\vec{x}$ is a covariant vector in a finite dimensional euclidean space, whereas $\partial_{\vec{x}}V(x)$ is the derivative (force) of a potential V. By means of this equation it is well known that it is possible to sample the equilibrium distribution $W_{eq}(x) = \exp(-\beta V(x))$ provided we satisfy the fluctuation dissipation theorem given by:

$$\langle\eta_i(t)\eta_j(t')\rangle = \delta(t - t')\delta_{i,j}\frac{2}{\beta} \tag{17}$$

Now we suppose to change the reference coordinate system by means of a generic transformation of variables $x \to \alpha$ (an $N-$ dimensional non linear mapping as in general relativity). Be the Jacobian of the transform given by the matrix L:

$$L_{i,j} = \partial_{x_j}\alpha_i(\vec{x}) \tag{18}$$

The Langevin equation in this new reference can be easily obtained:

$$\dot{\vec{\alpha}} = -S^{-1}\frac{\partial V}{\partial\vec{\alpha}} + L\vec{\eta} \tag{19}$$

where $S^{-1} = LL^\dagger$, and the equation (17) that defines the fluctuation dissipation theorem remains unchanged.

The Eq.(19) is covariant if we just replace the matrix S with the matrix defining the metric in a generic curved space:

$$ds^2 = S_{i,j}d\alpha_i d\alpha_j \tag{20}$$

where, as usual, in this formalism repeated indices are assumed summed. Indeed after the given transformation the above metric tensor transforms as:

$$S \to (L^\dagger)^{-1}SL^{-1} \tag{21}$$

that, as it should, leaves unchanged the covariant first order Langevin equation (19).

Thus, from the above equation, we obtain the desired result with the matrix L given by any solution of the matrix equation:

$$S^{-1} = LL^\dagger.$$

Unfortunately Eq. (19) looks a bit complicated when it is discretized in times $t_n = \Delta n$, because the integral of the random noise depends explicitly on the curvature of the non linear space by means of the matrix L, and the resulting integration is not univocally defined, simply because the solution $S^{-1} = LL^\dagger$ is not unique, since S^{-1} remains unchanged under the substitution $L \to LU$, where U is an arbitrary unitary matrix. In order to remove this arbitrariness, according to Risken[37], we can work out the integral of the equation of motion in a small time interval of length Δ, by requiring also that the corresponding Markov process:

$$
\begin{aligned}
\alpha(t_{n+1})^i &= \alpha(t_n)^i - \Delta\left[S^{-1}(t_n)\partial_{\vec{\alpha}}\left(V - \frac{1}{2\beta}\ln\text{Det}S\right)(t_n)\right]^i \\
&+ \frac{1}{2}\sum_k \partial_{\alpha_k}D_{i,k} + y_n^i \\
\langle y_n^i y_n^j\rangle &= D_{i,j} = \frac{2\Delta}{\beta}S_{i,j}^{-1}(t_n)
\end{aligned} \tag{22}
$$

has the correct equilibrium distribution for $\Delta \to 0$:

$$W_{eq}(\alpha) \propto \sqrt{\text{Det}S}\exp(-\beta V(\alpha)) \tag{23}$$

In fact it is possible to show that, only with the above definition of the drift term, the associated and univocally defined Fokker-Planck equation for the probability distribution $W(\alpha, t)$ reads for $\Delta \to 0$:

$$
\begin{aligned}
\partial_t W(\alpha, t) &= \sum_j \partial_j\left\{\sum_i \frac{1}{\beta}S_{j,i}^{-1}\partial_i W(\alpha, t)\right. \\
&+ \left. W(\alpha, t)\left[S^{-1}\partial_{\vec{\alpha}}\left(V(\alpha) - \frac{1}{2\beta}\ln\text{Det}S\right)\right]^j\right\}
\end{aligned} \tag{24}
$$

which has the equilibrium distribution $W_{eq}(\alpha)$ satisfying:

$$\sum_i \frac{1}{\beta}S_{j,i}^{-1}\partial_i W_{eq}(\alpha) + W_{eq}(\alpha)\sum_i S_{j,i}^{-1}\partial_i\left(V - \frac{1}{2\beta}\ln\text{Det}S\right) = 0 \tag{25}$$

Indeed, by multiplying both sides of the equations by $S_{k,j}$ and summing over j, we obtain the standard equation for the equilibrium distribution $\sqrt{|S|}\exp(-\beta V)$.

IV. COVARIANT LANGEVIN DYNAMICS FOR IONS AND ELECTRONS

We want to implement the above formalism in an ab-initio molecular dynamics (MD) at finite temperature dealing with electrons and ions within the same formalism, similarly to what was done in the pioneer work by R. Car and M. Parrinello[38]. In the following we will show how the ionic motion can be quite naturally included in the above scheme. In fact what we obtained before does not hold only for the electronic parameters, but for a generic set of parameters which appear in a variational wavefunction. The ionic positions $\mathbf{R}$ can thus be thought as complementary parameters. The inclusion of this kind of parameters in the above formalism is straightforward: if M is the number of atoms, then S becomes a $(p + 3M) \times (p + 3M)$ block-diagonal matrix. The mixed elements $S_{\{\alpha\},\{\mathbf{R}\}}$ are always zero since wave functions characterized by different sets of atomic positions are orthogonal. Moreover, since the ionic positions $\mathbf{R}$ belong to the real space, the corresponding metric is the Cartesian one, and is defined by a diagonal matrix $S(R_l, R_r) = S_N \delta_{l,r}$ among all the ion components. We can esplicitly write down the complete set of equations for both the atomic and electronic parameters. For the ionic positions we use

$$
\begin{aligned}
R(t_{n+1})^l &= R(t_n)^l + \Delta_N \ F^l(t_n, \{\alpha(t_n)\}) + \chi_n^l \\
\langle \chi_n^l \chi_n^r \rangle &= \frac{2\Delta_N}{\beta} \ \delta_{l,r}
\end{aligned}
\tag{26}
$$

with $l, r = 1, \cdots, 3M$ and F^l being the force acting on the l-th ionic cartesian coordinate, while for the electronic variables Eq. (22) holds with $i, j = 1, \cdots, p$ and where $-\partial_{\bar{\alpha}}V$ is the force acting on the parameters α, i.e, the gradient of the total electronic energy V evaluated at fixed $\mathbf{R}$ with respect to these parameters.

Notice also that the time discretization corresponding to the ionic dynamics is defined by the arbitrary constant S_N appearing in the extended metric tensor defined before, namely $\Delta_N = \Delta S_N^{-1}$. It is clear therefore that the relative speed between electron and ion dynamics can be tuned to optimize efficiency, exactly as in Car-Parrinello ab-initio molecular dynamics. We emphasize here that in the limit $\Delta, \Delta_N \to 0$ consistent results are obtained because the equilibrium distribution (23) remains unaffected by the choice of S_N.

V. RESULTS AND DISCUSSION

Once we set up the discretized equations (22,26) we can test the above formalism in a simple but realistic case. We are going to study the H_2 molecule, looking at the temperature behavior of the total energy E and the bond distance r between the two hydrogen atoms. We start with this simple system because the above quantities can be easily computed, providing therefore useful benchmarks for our technique.

According to App.C the distribution sampled by means of this covariant Langevin dynamics (CLD) represents an improvement of the BO only above a temperature T^*. At $T = 0$ our approximate free energy F_Q coincides with the BO one F_{BO}, but as soon as $T > 0$ the F_{BO} becomes better for $T \leq T^*$.

If the temperature is much lower than the electronic gap the BO approximation should be essentially exact and can be easily obtained from the potential energy surface (PES) $v(r)$ of the H_2 molecule.

In the following we are going to show that, in this simple system, we cannot distinguish the correct BO low temperature behavior and the one implied by our approximate technique, clearly indicating that T^* should be almost negligible for this system.

To proceed further we need now to specify what type of correlated variational wavefunction (4) we adopt in all the following calculations, and its dependence on the two electronic positions $\vec{r}_1$ and $\vec{r}_2$. In the singlet state the orbital function $f(\vec{r}_1, \vec{r}_2)$ is symmetric and positive and is parametrized here as a product of two factors $f(\vec{r}_1, \vec{r}_2) = f_0(\vec{r}_1, \vec{r}_2) \times \exp(J(\vec{r}_1, \vec{r}_2))$, where f_0 is taken fixed and allows to satisfy the electron-electron and electron-ion cusp conditions, whereas

$$
J = \sum_{i,j} \lambda_{i,j} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2)
\tag{27}
$$

is cusp free and is expanded systematically in a basis of atomic orbitals centered on each atom containing up to 3s and 1p gaussian functions and a constant one $\phi_0 = 1$. This amounts to $p = 65$ independent variational parameters for the symmetric matrix $\lambda_{i,j}$. The exponent of the gaussians are kept fixed during our simulations. Despite this limitation in the choice of the basis this is acceptable for the H_2 molecule in a physically relevant range of distances between the atoms, as it is shown in Fig.(1).

The chosen variational ansatz is particularly useful for evaluating the complicated terms in (22), i.e. the *drift-diffusion* ones which depend linearly from the temperature and require the knowledge of the derivative of the matrix

S. This is indeed simpler for the parameters $\lambda_{i,j}$ which appear in a linear fashion in the exponential factor J in Eq.(27). The first step is thus to construct the PES of the molecule (Fig.1). In this way we not only acquire the key information for the numerically exact evaluation of the BO observables, but we also check that our choice of the free variational parameters in the wave function allows us to recover the well known PES for this molecule[39, 40].
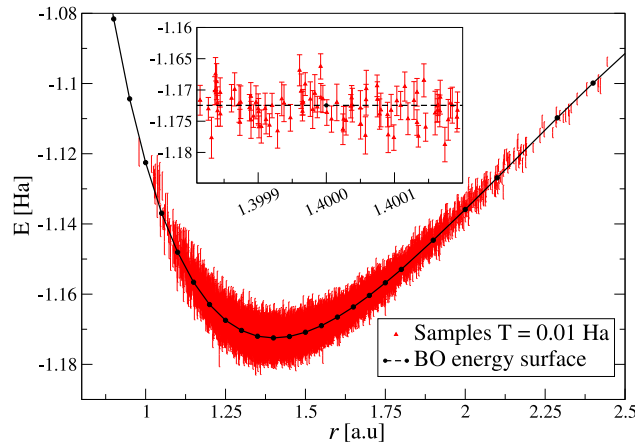

Figure 1: Black line: Total energy E as a function of the bond length r obtained by minimizing the energy of our variational wavefunction for fixed r; in doing this we act only on those parameters $\{\alpha\}$ which are kept free to evolve in the dynamics (22). Red points: Energy with error bars of configurations sampled in a dynamics (22,26) with $T = 0.01 \ Ha$. The PES is correctly followed during the simulation. In the inset a little region around the minimum at $r = 1.40 \ a.u.$ is enlarged.

Canonical averages of an observable $O(r)$ can be obtained by computing numerically the one dimensional (conditionally convergent) integrals

$$\hat{O} = \frac{\int dr \ r^2 \ O(r) \exp{(-\beta v(r))}}{\int dr \ r^2 \exp{(-\beta v(r))}} \tag{28}$$

On the other hand we can compute $\hat{O}$ as a time average on the Langevin dynamics (22,26) for sufficient low T. The extrapolation $\Delta \to 0$ involving the discretized time steps is performed in the order $\Delta_N \to 0, \Delta \to 0$. It is observed (see Fig.2) that the Δ_N dependence of the time averages of the quantities is linear for fixed Δ, a property useful in the extrapolation.

Finally we show our results for the total energy and the bond distance at varius temperatures in the range between $0.001 \div 0.01 \ Ha$, i.e. from room temperature to $\sim 3000 \ K$. The forces acting on the parameters and on the ions, as well as the matrix S are evaluated by a short QMC run at each iteration of the dynamics. In Fig.(3) and in Fig.(4) we show the outcome of our covariant Langevin dynamics simulations.

We see that our Langevin dynamics gives result in very good agreement with the expected BO values. We stress once again that this dynamics does not require an electronic minimization at each ionic move, realizing an impressive gain from the point of view of the computational cost. On the other hand, this kind of dynamics should behave differently with respect to the standard BO-MD one when the temperature is raised and for $T > T^*$ should be more realistic, because corresponding to a more accurate upper bound of the exact free energy F. In figures (3,4) we limit the study of the average energy and bond length in a range of temperatures smaller than 3000 K because, above this value, first dissociation events start to appear during the simulations. This temperature is in good qualitative agreement with low pressures experiments[41]. Roughly speaking the dissociation probability depends on the ratio between the thermal energy T and the depth of the free energy well ΔU through the Boltzmann weight[42] $\exp(-\Delta U/T)$ within the assumption that excited electronic eigenstates are well-separated in energy from the ground state. There are instead examples[22] in which BO approximation breaks down, particularly near the transition state of a chemical reaction. In fact, as the reaction coordinate r increases, the energy gap between the ground state and the first (antibonding) excited state becomes smaller[39], for example when $r > 4 \ a.u.$ this quantity becomes smaller than $8000K$. Therefore large fluctuations in the bond length, certainly occurring at large temperatures, are in principle not well described under a BO scheme. Since by definition, an atomic dissociation requires to sample correctly events with large r,
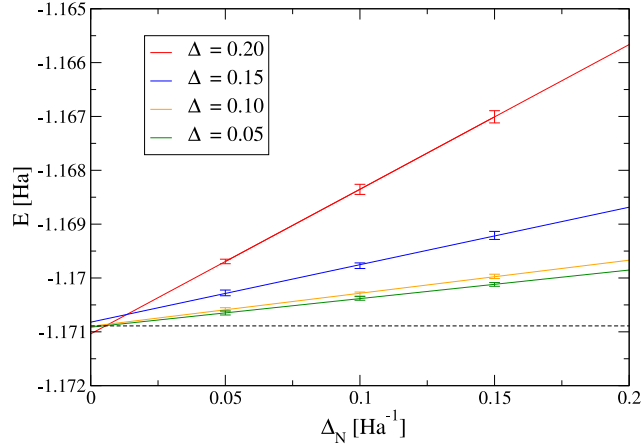
Figure 2: Time averages of the total energy E at $T = 0.003\ Ha$ as a function of Δ_N for 4 values of Δ. All the series converge roughly to the same value which is also the expected one (horizontal dashed line) obtained with eq. (28), simplifying the second extrapolation $\Delta \to 0$.
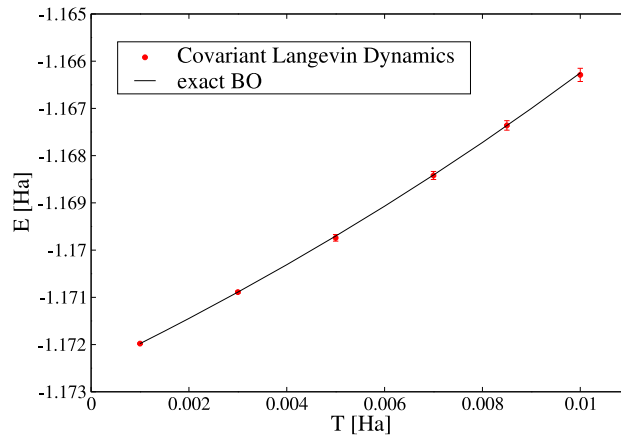

Figure 3: Total energy E as a function of temperature. The range of temperature is well below the electronic gap $\sim 0.17\ Ha$ (see Fig.1) so the expected exact value is the BO one evaluated by eq. (28) (black line). Red points are obtained by integrating the coupled equations (22,26). Data are in agreement with the predicted values.

we expect to find differences between the standard BO-MD and the dynamics generated by (22,26), at large enough temperatures. In Fig.5, we observe that the probability of dissociation is enhanced in our dynamics, which can take implicitely into account also the effective repulsion due to the antibonding state. As expected, this is in sharp contrast with a DFT-BO dynamics obtained using the QUANTUM ESPRESSO package[43, 44]. In the latter dynamics large fluctuations in r do not lead to dissociation, as is partially shown in fig. (5). Indeed no escape event occurs within DFT BO-MD, even for a long time dynamics. Moreover in order to compensate the well known overbinding error[45] of the local density approximation (LDA), we have increased the temperature by a factor proportional to the LDA energy barrier ($0.2415Ha$), and observed no qualitative changes in the trajectories, always confined around the minimum energy value. It is clear therefore that, quite generally, the BO-MD greatly underestimate the evaluation of the reaction rate if, for instance, a *mean first-passage time*[42] analysis is performed.
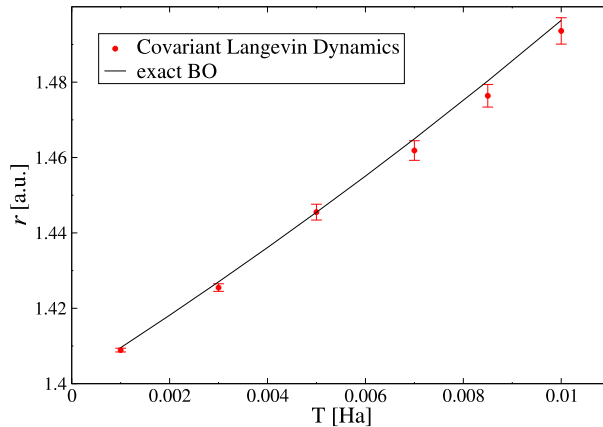
Figure 4: Bond length r as a function of temperature. Even for this observable the Langevin dynamics (red points) give values compatible with the expected ones (black line).
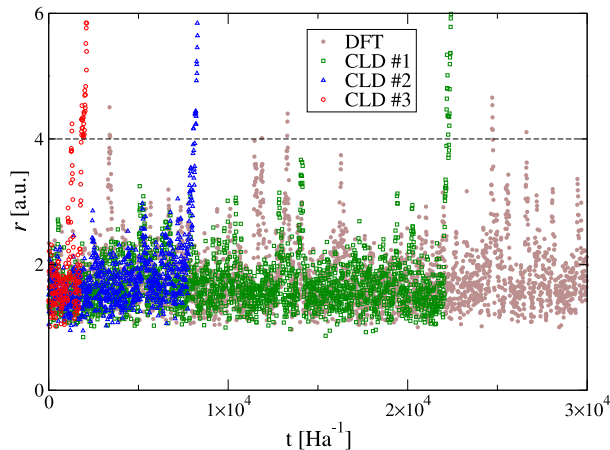

Figure 5: Bond length r as a function of simulation time at a temperature of $T = 8000\ K$. Coloured points (red, green and blue) correspond to simulation performed with the dynamics presented in this work, while the grey solid ones are obtained with a DFT- Langevin BOMD. The time step used in the integration of the equations is $\Delta_N = 0.1\ Ha^{-1}$ and points are plotted every 10 iterations. The dashed line indicates the distance r^* such that the energy gap between the ground state PES and the first excited one becomes smaller than T. All the CLD trajectories show escape events while the DFT one describes a stable molecular configuration up to $20 \times 10^4\ Ha^{-1}$ of simulation time (not shown).

VI.   CONCLUSIONS

In this paper we have introduced a new promising approach to deal with finite temperature simulations of electronic systems. The approach is general and, as we have emphasized in the introduction, can be easily extended to several branches of the electronic simulations, from ab-initio finite temperature simulation of realistic systems based on Hartree-Fock, DFT or quantum Monte Carlo methods, to finite temperature simulations of strongly correlated Hamiltonians defined on a lattice. In particular this technique allows us to improve systematically the Born-Oppenheimer approximation in a temperature range where the quantum effects on atoms are neglegible. In principle also these

quantum effects can be dealt in a simple way. To this purpose it is enough to define a quantum ansatz $|\alpha\rangle$ describing electrons and ion coordinates quantum mechanically, including in $\{\alpha\}$ also variational parameters corresponding to the atomic wave function $\Phi(\mathbf{R})$, for instance described by gaussians centered around the average atomic positions. In that case the same derivation holds as electrons and ions can be dealt in the same footing, the metric matrix S will have non trivial off diagonal elements between electronic and atomic variational parameters.

Although our first application is limited to the simple H_2 molecule with classical atomic coordinates, this extremely simple example already shows that it is possible to catch some qualitatively new behavior, that is not possible to describe with the conventional BO approximation. Namely at large enough temperature the molecule can dissociate due to non adiabatic effects.

We plan to extend our method to larger and more complex realistic systems including also quantum effects for atoms. Unfortunately, so far we have encountered a difficulty to compute in an efficient way the metric tensor S and its derivatives for a generic correlated wave function. For this reason, at present, it looks that the penalty method[34] could be a more realistic possibility for extending our technique, because the penalty method does not require the evaluation of the derivatives of the metric tensor. Apart for this technical issue there are many open problems that can be tackled with this new technique. For instance one would like to know the magnetic transition temperature of a piece of material. Without taking into account the electronic entropy this is not possible for most electronic ab-initio methods, but, by applying our technique, a reasonable estimate can be easily obtained. In lattice models, an old standing problem is for instance the extension of the Gutzwiller variational ansatz to finite temperature calculations. Within the variational Monte Carlo it has been established that the Hubbard model for U/t large enough should be superconducting with a d-wave order parameter. However it is not possible to predict within the same ansatz the much more interesting superconducting temperature and how it depends on the various details of the model, such as doping and the value of the Coulomb repulsion U/t. In our formulation what can be done at zero temperature can be readily extended to finite temperature and the evaluation of the critical temperature should be straightforward, likewise a standard (but much more accurate because including electron correlation) mean field theory at finite temperature.

Appendix A: Proof of the integral formula of Eq.(11)

In this appendix we use known results of differential geometry in Riemann spaces[46] with tensor metric S. In order to prove Eq.(11), it is enough to consider the complete basis:

$$|i\rangle = \prod_{n=1}^{N} c_{l_i(n)}^{\dagger}|0\rangle \tag{A1}$$

where $l_i(n)$ is an arbitrary choice of N different integers among the L possibilities, that defines the Hilbert of space of N fermions containing $D = \binom{L}{N}$ independent states. It is simple to realize that it is enough to prove that, given two arbitrary states $|i\rangle$ and $|j\rangle$, we have:

$$O_{i,j} = \int d\alpha^p \sqrt{|S|}\langle i|\alpha\rangle\langle\alpha|j\rangle = C\delta_{i,j} \tag{A2}$$

where C is an overall constant. Indeed, by assuming that the above equation holds, we can insert in Eq.(11) the completeness $I\sum_i |i\rangle\langle i|$ in both the bra and the ket of numerator in Eq.(11) and obtain:

$$\int d\alpha^p \sqrt{|S|}\langle\alpha|\exp(-\beta H_{\mathbf{R}})|\alpha\rangle =$$
$$\sum_{i,j}\langle j|\exp(-\beta H_{\mathbf{R}})|i\rangle \int d\alpha^p \sqrt{|S|}\langle\alpha|j\rangle\langle i|\alpha\rangle =$$
$$C\mathrm{Tr}\exp(-\beta H_{\mathbf{R}})$$

$$\tag{A3}$$

which easily proves Eq.(11).

In order to establish Eq.(A2) we can consider the group of transformations $\alpha \to \alpha'$ that leaves unchanged the metric tensor S defined by:

$$U|\alpha\rangle = |\alpha'\rangle \tag{A4}$$

where U is a unitary matrix that maps any variational ansatz α to a new variational ansatz α' of the form defined in Eq.(4). To this purpose it is enough to consider the unitary transformations defined by:

$$U_l c_m^\dagger U_l^\dagger = (1 - 2\delta_{l,m})c_m^\dagger, \ U_l = \exp(i\pi c_l^\dagger c_l) \tag{A5}$$
$$U_P c_l^\dagger U_P^\dagger = c_{p(l)}^\dagger \tag{A6}$$

where $p(l)$ is an arbitrary permutation of the L indices. All the above transformation are real and unitary and therefore conserve the distance between two arbitrary vectors, implying that the metric ds^2 remains unchanged under all these transformations, when applied to any arbitrary state of the ansatz:

$$ds^2 = S_{i,j}(\alpha)d\alpha^i d\alpha^j = S_{i,j}(\alpha')d\alpha'^i d\alpha'^j \tag{A7}$$

In differential geometry these transformations are called isometries, and represent the basis for the classification of symmetric Riemann spaces. In this context they are important to prove the main statement of this appendix. Indeed we can consider any isometry as a change of variable in the integral and obtain that (since the integration variables are dummy variables we can use α in place of α'):

$$O_{i,j} = \int d\alpha^p \sqrt{|S|}\langle i|U^\dagger|\alpha\rangle\langle\alpha|U|j\rangle \tag{A8}$$

Now since the set of states is complete the matrix elements $O_{i,j}$ define univocally an operator in the given $D-$ dimensional Hilbert space. Therefore by applying the relation (A8) for all isometries U_l for $l = 1, \cdots, L$, we obtain that this operator O commutes with all fermion occupation number n_l and therefore has to be diagonal, namely $O_{i,j} = C_i\delta_{i,j}$. On the other hand we can apply Eq.(A8) for an arbitrary unitary permutation U_P, that is able to connect any state i of the Hilbert space to any other one $|j\rangle$, namely $U_P|i\rangle = |j\rangle$. Thus it easily follows that:

$$O_{i,i} = \int d\alpha^p \sqrt{|S|}\langle i|U_P^\dagger|\alpha\rangle\langle\alpha|U_P|i\rangle \tag{A9}$$

$$= \int d\alpha^p \sqrt{|S|}\langle j|\alpha\rangle\langle\alpha|j\rangle = O_{j,j} \tag{A10}$$

implying that $O_{i,i} = C_i$ does not depend on i, and this concludes the proof of this appendix.

Appendix B: Proof of the upper bound for normalized states

The expectation value of an operator O over a normalized state α is equivalent to average $\langle\psi_i|O|\psi_i\rangle$ over the distribution $p_i = \langle\psi_i|\alpha\rangle^2$ over the eigenstates ψ_i of the operator O. In fact it immediately follows that $0 \le p_i \le 1$ and that $\sum_i p_i = 1$. Since for any distribution p_i and convex function f, it is well known that, from Jensen's inequality, we have:

$$\langle f(H)\rangle \ge f(\langle H\rangle) \tag{B1}$$

where the symbol $\langle O\rangle$ means averaging over the distribution p_i of the operator O, namely $\langle O\rangle = \sum_i p_i\langle\psi_i|O|\psi_i\rangle$. Since the operator H is Hermitian, H and $f(H)$ are diagonalized by the same eigenvectors, and therefore the distribution p_i is the same for both operators and relation (B1) simply follows from the convexity of f. Then by using the convexity of the function $f(x) = \exp(-x/T)$, by applying the above consideration to the operator $O = f(H)$, we obtain:

$$\langle\alpha|\exp(-H/T)|\alpha\rangle \ge \exp(\langle\alpha|-H/T|\alpha\rangle) \tag{B2}$$

which concludes the proof of this appendix.

Appendix C: Approximate partition function Z_Q versus exact and Born-Oppenheimer partition functions

In this appendix we want to investigate the nature of the approximation of the partition function Z_Q defined in (12) and used in this work. In order to do this we will compare the approximate partition function Z_Q with the exact Z and the approximate Born-Oppenheimer Z_{BO}, in the general case when we use $p < D$ variational parameters in the normalized wave function ansatz $|\alpha\rangle$. To simplify the notations we avoid to use the dependence on the atomic positions R. We assume that the ground state energy E_0 is non degenerate and all the eigenvalues $|E_i| \leq B$, namely the spectrum is bounded and B, as well as the maximum gap $\Delta = \text{Max}_i E_i - E_0$, grows at most linearly with the number N of electrons. These assumptions are commonly satisfied by physical Hamiltonians of interacting fermions.

Within these assumptions, we will see that $Z_Q(T)$ is an approximation for $Z(T)$ better than $Z_{BO}(T)$ as long as the temperature T is larger than a crossover temperature $T^* < \bar{T}$ where $\bar{T}$ remains finite for $N \to \infty$.

As mentioned, we assume to know a complete orthonormal set $\{|i\rangle\}_{i=0,\ldots,D-1}$ of eigenstates of the hamiltonian H that operates in a D-dimensional Hilbert space. This implies that at a given temperature T the exact partition function is:

$$Z(T) = \sum_{i=0}^{D-1} e^{-E_i/T} \tag{C1}$$

whereas the BO partition function is:

$$Z_{BO}(T) = \exp(-E_V/T) \tag{C2}$$

where $E_V = \text{Min}_\alpha \langle \alpha|H|\alpha\rangle$ and the approximate partition function Z_Q is given in Eq.(12). We remind that we have already proven, using the convexity of the exponential function, that the relation:

$$Z(T) \geq Z_Q(T) \tag{C3}$$

holds for every T, and obviously $Z(T) \geq Z_{BO}(T)$.

In order to identify the more accurate approximate partition function, namely the one with the larger bound for $Z(T)$ we consider the ratio between the Z_Q and Z_{BO}:

$$\zeta_Q(T) \equiv \frac{Z_Q(T)}{Z_{BO}(T)} \tag{C4}$$

Since $Z_Q(T)$ is essentially a classical partition function over p variables, the equipartition theorem immediately implies that:

$$Z_Q(T) \propto Z_{BO}(T)T^{p/2} \tag{C5}$$

Thus the BO approximation is better at low enough temperature, and, our low temperature free energy $F_Q = E_V - p/2T \ln T$ is expected to be a very bad approximation of the quantum free energy especially when p is very large, just because classical and quantum free energy differ substantially at very low temperatures.

The above consideration could lead to the disappointing conclusion that $\zeta_Q(T) > 1$, namely $F_Q(T) \leq E_V$, only for very high temperatures.

However we can easily find a lower bound for $\zeta_Q(T)$ by using that the spectrum is bounded, as assumed at the beginning of this appendix:

$$\zeta_Q(T) = D\frac{\int d\alpha^p \sqrt{|S|} \exp(-\frac{\langle \alpha|H - E_V|\alpha\rangle}{T})}{\int d\alpha^p \sqrt{|S|}} \geq D \exp(-\Delta/T) \tag{C6}$$

When the above bound is larger than one, $\zeta_Q(T)$ is certainly larger than one, implying $F_Q \leq F_{BO}$. This occurs for $T \geq \bar{T}$, where $\bar{T}$ is easily determined by $\bar{T} = \Delta/\ln D$. Hence in the thermodynamic limit there exists a finite crossover temperature T^*, as $\Delta/\ln D$ remains finite for $N \to \infty$, according to our assumptions.

Appendix D: Slater determinants and symmetric Riemann spaces

We consider the space $\mathcal{M}$ of normalized Slater determinants in a finite dimensional Hilbert space $\mathcal{H}$ where fermions can occupy L different one particle states, denoted by conventional creation operators $c_i^\dagger$. A Slater determinant with

N electrons can be formally written in second quantization notations by means of $N \times L$ real numbers ψ_j^i:

$$|\psi\rangle = \prod_{i=1}^{N} \sum_{j=1}^{L} \psi_{i,j} c_j^\dagger |0\rangle \tag{D1}$$

However all the variables of the matrix ψ are highly redundant because, as well known, the Slater determinant after the linear transformations $\psi \to \hat{L}\psi$ is multiplied by a constant $|\psi\rangle \to |\hat{L}||\psi\rangle$, where $\hat{L}$ is an arbitrary $N \times N$ matrix and $|\hat{L}|$ its determinant. It is clear that, in order to define a Slater determinant with unit norm we can consider one constraint $\langle\psi|\psi\rangle = |\psi\psi^\dagger| = 1$ over the NL variables defining the $N \times L$ matrix ψ, amounting therefore to $NL - 1$ independent real variables. By the above discussion, the wavefunction $|\psi\rangle$ is left invariant for all matrix transformation $\psi \to \hat{L}\psi$ with $|\hat{L}| = 1$, defining $N^2 - 1$ independent variables for $\hat{L}$. Thus, it follows that $|\psi\rangle$ can be parametrized by $(NL - 1) - (N^2 - 1) = N(L - N)$ independent real variables. In a more rigourous mathematical formalism, by neglecting an immaterial overall sign ± 1 in the definition of ψ, the space $\mathcal{M}$ represents the coset space $O(L, L - N)$, where $O(L, L - N)$ is the irreducible symmetric Riemannian space $SO(L)/S(O(N) \times O(L - N))$.[46] We remind here that $O(N)$ denotes the group of generic orthogonal matrices, whereas $SO(N)$ represents the group of orthogonal matrices with determinant one. Similarly $O(N) \times O(L - N)$ represents the group of block diagonal matrices with $N \times N$ and $L - N \times L - N$ blocks, where each block is in turn an orthogonal matrix. Also the symbol $S(O(N) \times O(L - N))$ indicates that the determinant of this block diagonal matrix (the products of the determinant of each block, equal to ± 1 as for any orthogonal matrix) has to be 1.

This space $\mathcal{M}$ is compact (all the $N(L - N)$ independent variables represent essentially angles of unit vectors in L dimensional space) and there exist a unique (up to a constant) measure $d\mu$ such that $d\bar{U}\mu = d\mu$ for all $\bar{U} \in SO(L)$ where $SO(L)$ is the group of $L \times L$ orthogonal matrices with unit determinant[46], namely $|\bar{U}| = 1$. An orthogonal matrix U, acts on $|\psi\rangle$ in an obvious way, namely $\psi \to \psi U$ in Eq.(D1). The space $\mathcal{M}$ can be therefore represented by an irreducible symmetric Riemannian space. Using a matrix $U \in SO(L)$ we have essentially L orthonormal directions (e.g. the raws of the matrix), and the first N spans all possible Slater determinants in the space $\mathcal{M}$. For the previous discussion this Slater determinant will be left unchanged (up to a sign) if we multiply the matrix U for an arbitrary element of the $S(O(N) \times O(L - N))$ unitary group, and therefore $\mathcal{M}$ is equivalent to the space $SO(L)/S(O(N) \times O(L - N))$.

As a further proof that $\mathcal{M}$ is equivalent to $SO(L)/S(O(N) \times O(L - N))$ it is also easy to verify that the dimension of this space space is exactly $N(L - N)$. The dimension of an orthogonal matrix of dimension D is $D(D - 1)/2$, and therefore the dimension of the coset space $SO(L)/S(O(N) \times O(L - N))$ is $L(L - 1)/2 - (L - N)(L - N - 1)/2 - N(N - 1)/2 = N(L - N)$■.

In order to represent the irreducible space $SO(L)/S(O(N) \times O(L - N))$ for $L >> N$, with $N(L - N)$ variables, a possible choice is to define an unconstrained $N \times (L - N)$ matrix V and the corresponding unitary $L \times L$ matrix Q:

$$Q = \begin{pmatrix} \sqrt{I - VV^\dagger} & V \\ -V^\dagger & \sqrt{I - V^\dagger V} \end{pmatrix} \tag{D2}$$

with the constraint that the positive definite matrix $VV^\dagger$ has all eigenvalues bounded by one, namely $VV^\dagger \leq 1$. Thus we explicitly see that the space is compact. As mentioned before we can identify a wavefunction $\psi \in M$ with the first N raws of this unitary matrix Q, up to a sign, so that the orbitals of the determinant are:

$$\psi_{l,k} = Q_{l,k} \text{ for } l = 1, 2, \cdots, N. \tag{D3}$$

A measure $d\psi$ of the coset (reducible) Riemann space $SO(L)/S(O(N) \times O(L - N))$ is said to be an invariant measure when it remains invariant under all unitary transformations $U \in U(L)$, namely $d\psi U = d\psi$. An invariant measure represented by the matrix V is given by:

$$d\psi = C d\mu(V) \tag{D4}$$

where C is an appropriate normalization constant, and $\mu(V)$ is the invariant measure in $SU(L)/S(U(N) \times U(L - N))$.[46] Although explicit formulas are known for the invariant measure, they look a bit complicated to be implemented in practice. We are confident that a very convenient expression of the invariant measure is possible in terms of the eigenvalues of $VV^\dagger$, which should amount to only N^3 operations. This would lead immediately to a computationally affordable extension of our method to DFT or mean-field type of ansatz.

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